

CLAIMS

We Claim:

5 1. A method for lowering the sulfur content of a naphtha hydrocarbon feed stream while substantially maintaining the yield of olefin compounds in the feed stream, said method comprising

10 i) contacting a naphtha feed with a membrane separation zone, said separation zone containing a membrane having a sufficient flux and selectivity to separate a sulfur-enriched permeate fraction and a sulfur deficient retentate fraction, said membrane having a sulfur enrichment factor of greater than 1.5, said naphtha feed comprising sulfur containing aromatic hydrocarbons, sulfur containing non-aromatic hydrocarbon and olefin compounds, said sulfur enriched permeate fraction being enriched in sulfur containing aromatic hydrocarbons and sulfur containing non-aromatic hydrocarbons as compared to the naphtha feed;

15 ii) recovering the sulfur deficient retentate fraction as a product stream;

 iii) subjecting the sulfur enriched permeate fraction to a non-membrane process to reduce sulfur content; and

20 iv) recovering the reduced sulfur permeate product stream, wherein the total amount of olefin compounds present in the retentate product stream and the permeate product stream is at least 50 wt % of olefin compound present in the feed.

25 2. The method of claim 1 wherein the membrane is an asymmetric membrane selected from the group consisting of a polyimide membrane, a polyurea-urethane membrane and a polysiloxane membrane.

 3. The method of claim 1 wherein the membrane is a polyimide membrane.

4 The method of claim 1 wherein the membrane is a polyurea urethane membrane.

5 5. The method of claim 1 wherein the membrane is a polysiloxane membrane.

6. The method of claim 1 wherein the sulfur content of the sulfur deficient retentate fraction is less than 100 ppm.

10 7. The method of claim 6 wherein the sulfur content of the sulfur deficient fraction is less than 50 ppm.

8. The method of claim 6 wherein the sulfur content of the sulfur deficient retentate fraction is less than 30 ppm.

15 9. The method of claim 1 wherein the naphtha feed stream is a cracked naphtha.

10. The method of claim 9 wherein the naphtha is a FCC naphtha.

20 11. The method of claim 10 wherein the naphtha is a FCC light cat naphtha having a boiling range from about 50°C to about 105°C.

12. The method of claim 1 wherein the naphtha is a coker naphtha.

25 13. The method of claim 1 wherein the naphtha is a straight run.

14. The method of claim 1 wherein the sulfur deficient retentate fraction comprises at least 50 wt % of the total feed.

15. The method of claim 14 wherein the sulfur deficient retentate fraction comprises at least 70 wt % of the total feed.

5 16. The method of claim 1 wherein the membrane separation zone operates under pervaporation conditions.

17. The method of claim 1 wherein the membrane separation zone operates under perstraction conditions.

10 18. The method of claim 1 wherein the sulfur-enriched permeate fraction is subjected to a hydrotreating process to reduce sulfur content.

15 19. The method of claim 1 wherein the sulfur-enriched permeate fraction is subjected to an adsorption process to reduce sulfur content.

20 20. The method of claim 1 wherein the sulfur-enriched permeate fraction is subjected to a catalytic distillation process to reduce sulfur content.

21. The method of claim 1 wherein the membrane has a sulfur enrichment factor of greater than 2.

22. The method of claim 1 wherein the membrane has a sulfur enrichment factor ranging from about 2 to about 20.

25 23. The method of claim 1 wherein the total amount of olefin compounds in the retentate product stream and the permeate product stream is from about 50 to about 90 wt % of olefin compounds present in the feed.

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24. A method for lowering the sulfur content of a naphtha hydrocarbon feed stream while substantially maintaining the yield of olefin compounds in the feed stream, said method comprising

5 i) contacting a naphtha feed with a membrane separation zone, said separation zone containing a polyimide membrane having a sufficient flux and selectivity to separate a sulfur-enriched permeate fraction and a sulfur deficient retentate fraction under pervaporation conditions, said naphtha feed comprising sulfur containing aromatic hydrocarbons, sulfur containing non-aromatic hydrocarbons and olefin compounds, said sulfur enriched permeate fraction being enriched in sulfur containing aromatic
10 hydrocarbons and sulfur containing non-aromatic hydrocarbons as compare to the naphtha feed;

ii) recovering the sulfur deficient retentate fraction as a product stream;

iii) subjecting the sulfur-enriched permeate fraction to a non-membrane process to reduce sulfur content; and

15 iv) recovering the reduced sulfur permeate product stream, wherein the total amount of olefin compounds present in the retentate product stream and the permeate product stream is at least 50 wt % of olefin compounds present in the feed.

25. The method of claim 24 wherein the membrane is one having a sulfur enrichment factor of greater than 1.5.
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3 26. The method of claim 24 wherein the sulfur content of the sulfur deficient retentate fraction is less than 100 ppm.

4 27. The method of claim 26 wherein the sulfur content of the sulfur deficient fraction is less than 50 ppm.
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28. The method of claim ~~26~~³ wherein the sulfur content of the sulfur deficient retentate fraction is less than 30 ppm.

29. The method of claim ~~24~~⁶ wherein the naphtha feed stream is a cracked naphtha.

30. The method of claim ~~29~~⁶ wherein the naphtha is a FCC naphtha.

31. The method of claim ~~30~~⁷ wherein the naphtha is a FCC light cat naphtha having a boiling range from about 50°C to about 105°C.

32. The method of claim ~~24~~¹ wherein the naphtha is a coker naphtha.

33. The method of claim ~~24~~¹ wherein the naphtha is a straight run.

34. The method of claim ~~24~~¹¹ wherein the sulfur deficient retentate fraction comprises at least 50 wt % of the total feed.

35. The method of claim ~~34~~¹¹ wherein the sulfur deficient retentate fraction comprises at least 70 wt % of the total feed.

36. The method of claim 24 wherein the sulfur-enriched permeate fraction is subjected to a hydrotreating process to reduce sulfur content.

37. The method of claim 24 wherein the sulfur-enriched permeate fraction is subjected to an adsorption process to reduce sulfur content.

38. The method of claim ~~24~~² wherein the sulfur-enriched permeate fraction is subjected to a catalytic distillation process to reduce sulfur content.

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~~39~~². The method of claim ~~25~~² wherein the membrane has a sulfur enrichment
5 factor of greater than 2.

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~~40~~². The method of claim ~~25~~² wherein the membrane has a sulfur enrichment
factor ranging from about 2 to about 20.

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10 ~~41~~¹. The method of claim ~~24~~¹ wherein the sulfur deficient retentate fraction
contains from about 50 to about 90 wt % of olefin compounds present in the initial feed.

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42. A method for lowering the sulfur content of a naphtha hydrocarbon feed
stream while substantially maintaining the yield of olefin compounds in the feed stream,
15 said method comprising

- 20 i) contacting a naphtha feed with a membrane separation zone, said separation
zone containing a polysiloxane membrane having a sufficient flux and selectivity to
separate a sulfur-enriched permeate fraction and a sulfur deficient retentate fraction under
pervaporation conditions, said naphtha feed comprising sulfur containing aromatic
hydrocarbons, sulfur containing non-aromatic hydrocarbons and olefin compounds, said
sulfur enriched permeate fraction being enriched in sulfur containing aromatic
hydrocarbons and sulfur containing non-aromatic hydrocarbons as compared to the
naphtha feed;
- 25 ii) recovering the sulfur deficient retentate fraction as a product stream;
- iii) subjecting the sulfur-enriched permeate fraction to a non-membrane process
to reduce sulfur content; and

iv) recovering the reduced sulfur permeate product stream, wherein the total amount of olefin compounds present in the retentate product stream and the permeate product stream is at least 50 wt % of olefin compounds present in the feed.

5 ²²~~43~~. The method of claim ²¹~~42~~ wherein the membrane is one having a sulfur enrichment factor of greater than 1.5.

²³~~44~~. The method of claim ²¹~~42~~ wherein the sulfur content of the sulfur deficient retentate fraction is less than 100 ppm.

10 ²⁴~~45~~. The method of claim ²³~~44~~ wherein the sulfur content of the sulfur deficient fraction is less than 50 ppm.

15 ²⁵~~46~~. The method of claim ²³~~45~~ wherein the sulfur content of the sulfur deficient retentate fraction is less than 30 ppm.

²⁶~~47~~. The method of claim ²¹~~42~~ wherein the naphtha feed stream is a cracked naphtha.

20 ²⁷~~48~~. The method of claim ²⁶~~47~~ wherein the naphtha is a FCC naphtha.

²⁸~~49~~. The method of claim ²⁷~~48~~ wherein the naphtha is a FCC light cat naphtha having a boiling range from about 50°C to about 105°C.

25 ²⁹~~50~~. The method of claim ²¹~~42~~ wherein the naphtha is a coker naphtha.

³⁰~~51~~. The method of claim ²¹~~42~~ wherein the naphtha is a straight run.

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52. The method of claim 21 wherein the sulfur deficient retentate fraction comprises at least 50 wt % of the total feed.

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53. The method of claim 21 wherein the sulfur deficient retentate fraction
5 comprises at least 70 wt % of the total feed.

54. The method of claim 42 wherein the sulfur-enriched permeate fraction is subjected to a hydrotreating process to reduce sulfur content.

55. The method of claim 42 wherein the sulfur-enriched permeate fraction is subjected to an adsorption process to reduce sulfur content.

56. The method of claim 42 wherein the sulfur-enriched permeate fraction is subjected to a catalytic distillation process to reduce sulfur content.

57. The method of claim 42 wherein the membrane has a sulfur enrichment factor of greater than 2.

58. The method of claim 43 wherein the membrane has a sulfur enrichment factor ranging from about 2 to about 20.

59. The method of claim 42 wherein the sulfur deficient retentate fraction contains from about 50 to about 90 wt % of olefin compounds present in the initial feed.

60. A method for lowering the sulfur content of a naphtha hydrocarbon feed stream while substantially maintaining the yield of olefin compounds in the feed stream, said method comprising

i) contacting a naphtha feed with a membrane separation zone, said separation zone containing a polyurea urethane membrane having a sufficient flux and selectivity to separate a sulfur-enriched permeate fraction and a sulfur deficient retentate fraction under pervaporation conditions, said naphtha feed comprising sulfur containing aromatic hydrocarbons, sulfur containing non-aromatic hydrocarbons and olefin compounds, said sulfur enriched permeate fraction being enriched in sulfur containing aromatic hydrocarbons and sulfur containing non-aromatic hydrocarbons as compared to the naphtha feed;

ii) recovering the sulfur deficient retentate fraction as a product stream;

iii) subjecting the sulfur-enriched permeate fraction to a non-membrane process to reduce sulfur content; and

iv) recovering the reduced sulfur permeate product stream, wherein the total amount of olefin compounds present in the retentate product stream and the permeate product stream is at least 50 wt % of olefin compounds present in the feed.

61. The method of claim 60 wherein the membrane is one having a sulfur enrichment factor of greater than 1.5.

62. The method of claim 60 wherein the sulfur content of the sulfur deficient retentate fraction is less than 100 ppm.

63. The method of claim 62 wherein the sulfur content of the sulfur deficient fraction is less than 50 ppm.

64. The method of claim 63 wherein the sulfur content of the sulfur deficient retentate fraction is less than 30 ppm.

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65. The method of claim 41 wherein the naphtha feed stream is a cracked naphtha.

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66. The method of claim 46 wherein the naphtha is a FCC naphtha.

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67. The method of claim 47 wherein the naphtha is a FCC light cat naphtha having a boiling range from about 50°C to about 105°C.

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68. The method of claim 41 wherein the naphtha is a coker naphtha.

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A8 69. The method of claim 60 wherein the naphtha is a straight run.

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70. The method of claim 41 wherein the sulfur deficient retentate fraction comprises at least 50 wt % of the total feed.

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71. The method of claim 51 wherein the sulfur deficient retentate fraction comprises at least 70 wt % of the total feed.

72. The method of claim 60 wherein the sulfur-enriched permeate fraction is subjected to a hydrotreating process to reduce sulfur content.

73. The method of claim 60 wherein the sulfur-enriched permeate fraction is subjected to an adsorption process to reduce sulfur content.

25 74. The method of claim 60 wherein the sulfur-enriched permeate fraction is subjected to a catalytic distillation process to reduce sulfur content.

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75. The method of claim 41 wherein the membrane has a sulfur enrichment factor of greater than 2.

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76. The method of claim 54 wherein the membrane has a sulfur enrichment factor ranging from about 2 to about 20.

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77. The method of claim 46 wherein the sulfur deficient retentate fraction contains from about 50 to about 90 wt % of olefin compounds present in the initial feed.

10 78. The method of claim 1 further comprising combining the sulfur deficient retentate product stream and the reduced sulfur permeate product stream.

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79. The method of claim 24 further comprising combining the sulfur deficient retentate product stream and the reduced sulfur permeate product stream.

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80. The method of claim 21 further comprising combining the sulfur deficient retentate product stream and the reduced sulfur permeate product stream.

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81. The method of claim 41 further comprising combining the sulfur deficient retentate product stream and the reduced sulfur permeate product stream.

82 A method for lowering the sulfur content of a naphtha hydrocarbon feed stream while substantially maintaining the yield of olefin compounds in the feed stream, said method comprising

25 i) contacting a naphtha feed with a membrane separation zone, said separation zone containing a membrane having a sufficient flux and selectivity to separate a sulfur-enriched permeate fraction and a sulfur deficient retentate fraction, said sulfur deficient retentate fraction comprising at least 50 wt % of the naphtha feed, said membrane having

a sulfur enrichment factor of greater than 1.5, said naphtha feed comprising sulfur containing aromatic hydrocarbons, sulfur containing non-aromatic hydrocarbons and olefin compounds, said sulfur enriched permeate fraction being enriched in sulfur containing aromatic hydrocarbons and sulfur containing non-aromatic hydrocarbons as compared to the naphtha feed;

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ii) recovering the sulfur deficient retentate fraction as a product stream;
iii) subjecting the sulfur enriched permeate fraction to a non-membrane process to reduce sulfur content; and

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iv) recovering the reduced sulfur permeate product stream, wherein the total amount of olefin compounds present in the retentate product stream and the permeate product stream is at least 50 wt % of olefin compound present in the feed.

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